Electron Transfer through a Carbon–Carbon Triple Bond: Kinetics and Mechanisms of the Reductions of μ-(Carboxyacetylenecarboxylato-*OO′*)-di-μ-hydroxo-bis[triamminecobalt(III)] and Related Complexes by Chromium(II) and Vanadium(II)

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Four polynuclear cobalt(III)ammine complexes with bridging carboxylic acids containing a carbon–carbon triple-bond have been prepared and characterized. The kinetics of the reduction of the μ-(carboxyacetylenecarboxylato-*OO′*)-di-μ-hydroxo-bis[triamminecobalt(III)] complex, (I), by Cr^{II} has been studied in perchloric acid media. Reduction of the first Co^{III} is rate determining and dependent on $[H^+]$. It is shown that both the protonated and unprotonated form of complex (I) are reduced by an inner-sphere mechanism with attack of the first Cr^{2+} at the uncomplexed remote carbonyl oxygen and transfer of an electron through the ligand. The detection of a binuclear chromium(III) complex incorporating the organic ligand as a product of the reaction is strong evidence that the second Co^{III} is reduced *via* an inner-sphere mechanism too, most probably by attack of a second Cr^{2+} at the carbonyl oxygen adjacent to co-ordinated Co^{III}. The assignments are supported by reactivity patterns observed for the reductions of similar complexes: di-μ-hydroxo-μ-(methoxycarbonylacetylenecarboxylato-*OO′*)-bis-[triamminecobalt(III)], (II), reacts with Cr^{2+} by an inner-sphere mechanism with remote attack, but the rate of reduction is independent of $[H^+]$; V^{2+} reacts *via* an outer-sphere mechanism. The reductions of complexes μ-(acetylenedicarboxylato-$O^1O^{1'}$: $O^2O^{2'}$)-bis{di-μ-hydroxo-bis[triamminecobalt(III)]}, (III), and di-μ-hydroxo-μ-(propiolato-*OO′*)-bis[triamminecobalt(III)], (IV), by Cr^{2+} and V^{2+} occur by outer-sphere mechanisms, respectively, because a suitable ‘ lead-in ’ functional group for the reductants is not available. No evidence for direct interactions of the reductants with the C≡C triple-bonds has been found.

BINUCLEAR cobalt(III) ammine complexes with μ-carboxylato-bridging ligands represent a useful class of compounds for studies on electron-transfer reactions through extended organic structural units.[1-3] Inner-sphere reductions of these complexes by aquametal ions such as $[Cr(OH_2)_6]^{2+}$ or to a much lesser extent $[V(OH_2)_6]^{2+}$ occur exclusively *via* remote attack of the reductant if the organic ligand bears a suitable ‘ lead-in ’ function (*e.g.* a carboxyl or aldehyde group) and if the ligand is capable of ‘ mediating ’ an electron. Thus, structural factors governing the capacity of a given carboxylic acid to mediate electrons can easily be investigated without the complication of other rapid parallel inner-sphere reaction paths.

It has previously been demonstrated that a carbon–carbon double-bond (fumaric and maleic acids being the investigated ligands) readily mediates an electron,[4,5] whereas a saturated carbon atom (malonic acid) appears to act as an ‘ insulator ’ since the di-μ-hydroxo-μ-malonato-bis[triamminecobalt(III)] complex is reduced by Cr^{2+} *via* an outer-sphere mechanism [6] (see Table 6). In the present work we have studied the possibility of transferring an electron through a C≡C triple-bond which has not been done previously. We report here details of the preparation and characterization, and the kinetics of the reductions, of complexes (I)—(IV) by Cr^{2+} and V^{2+}.

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[1] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1832.

[2] A. G. Sykes, *Chem. in Britain*, 1974, **10**, 170.

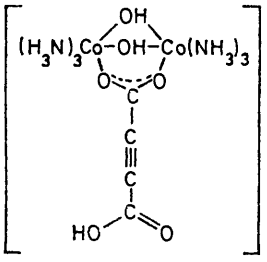
[3] K. Wieghardt and A. G. Sykes, *J.C.S. Dalton*, 1974, 651.

[4] For mononuclear $Co(NH_3)_5$ derivatives this behaviour has been reported by D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, 1961, **83**, 1785; J. K. Hurst and H. Taube, *ibid.*, 1968, **90**, 1178.

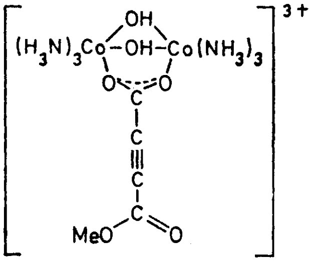
[5] M. R. Hyde, K. L. Scott, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, 1976, 153.

[6] B. Kipling, M. Hery, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, in the press.

RESULTS



(I)



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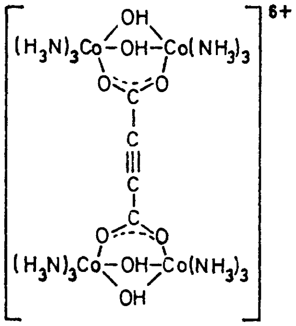

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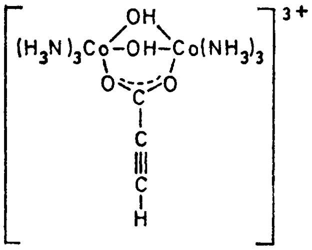


(IV)

Reduction of μ-(Carboxyacetylenecarboxylato-OO′)-di-μ-hydroxo-bis[triamminecobalt(III)], (I), *by* Cr^{2+}.—The overall stoicheiometry of the reaction of complex (I) with Cr^{2+} was 4 : 1 (3.8 ± 0.1 mol of Cr^{2+} to 1 mol of complex). Plots of absorbance against time for reaction mixtures with an excess of Cr^{2+} (followed at 524 nm) showed a rapid and large decrease in absorbance which could be attributed to the reduction of two cobalt(III) ions, and a consecutive very slow increase in absorbance which is due to further production of Cr^{III} *via* reduction of the organic ligand. From ion-exchange separations of 2 : 1 reaction mixtures (2 mol of Cr^{2+} to 1 mol of complex), 98% of the initial Co^{III} was recovered as $[Co(OH_2)_6]^{2+}$ indicating that the first rapid stage of the reaction accounts for the reduction of two Co^{III} as in (1). Reaction

$$2Cr^{2+} + Co^{III}_2 \longrightarrow 2Cr^{III} + 2Co^{2+} \qquad (1)$$

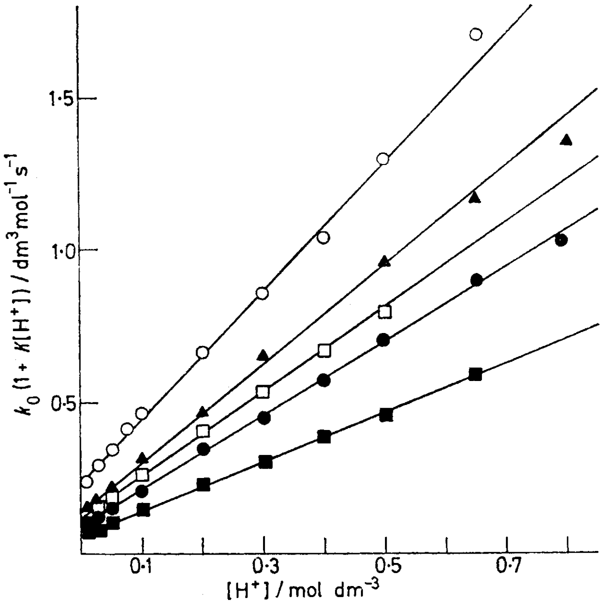
mixtures containing an eight-fold excess of Cr^{2+} were allowed to react until no spectral changes could be detected. Then the excess of Cr^{2+} was oxidized by passing a stream of oxygen through the solution. In order to separate organic materials from metal ions, complexes containing the organic ligand were destroyed by base hydrolysis. The ligand was extracted from re-acidified solutions with diethyl ether. A colourless precipitate was recovered from the ether phase, and was identified by its i.r. spectrum and melting point as fumaric acid. This is in agreement with results of Bottei and Joern [7] who reported that uncomplexed acetylenedicarboxylic acid (hereafter referred to as H_2acd) is reduced by Cr^{2+} yielding fumaric acid.

The second stage of the reaction is sufficiently slow that it does not interfere significantly with the reduction of the cobalt(III) centres. It is possible to obtain good pseudo-first-order rate constants for the first stage of the reaction from plots of log ($D_t - D_\infty$) against time where D_∞ is the absorbance after six half-lives of the first stage and D_t that after time t. Such plots were linear to greater than 95% completion of the first stage. The kinetics of the second slow stage were not investigated since the precise nature of the reactants involved are not known.

The first rapid stage proceeds in two steps, each involving attack of Cr^{2+} and reduction of one Co^{III}, reduction of the first Co^{III} being rate determining. The rate of reduction is enhanced at high [H^+] and follows the rate law (2), indicating that both protonated (k_a) and unprotonated (k_b) forms of

$$\frac{1}{[Cr^{2+}]}\cdot\frac{d\ln[Co^{III}_2]}{dt} = k_0 = \frac{k_aK[H^+] + k_b}{1 + K[H^+]} \qquad (2)$$

complex (I) participate (K is the equilibrium constant for the protonation). As shown in the Figure, good linear behaviour of $k_0(1 + K[H^+])$ with [H^+] was found using a value of 2.5 dm^3 mol^{-1} for K at the different temperatures. Second-order rate constants, k_0, are listed in Table 1, values of k_a and k_b at 25 °C and the respective activation parameters are given in Table 3. The latter were computed using a non-linear least-squares program in which each data point was given equal weighting and K was assumed to be independent of temperature.[8] From spectrophotometric measurements on the complex in perchloric acid solutions at 15, 25, and 35 °C and an ionic strength of 1.0 mol dm^{-3} ($Li[ClO_4]$), values of an apparent protonation constant K = 2.1 ± 0.5 dm^3 mol^{-1} were determined. The largest difference in the spectrum of the complex as a function of [H^+] occurred at 250 nm and is too small to enable precise measurements to be made. Within experimental error, K did not show a dependence on temperature. It is concluded that the measured equilibrium constant and the kinetically determined value of K are in satisfactory agreement.



Dependence of k_0 on [H^+] for the Cr^{2+} reduction of complex (I) at different temperatures: (■) 4.8, (●) 14.9, (□) 20.0, (▲) 25.0, and (○) 35.0 °C

In order to determine the reaction products, *ca.* 2 : 1 reactant mixtures (Cr^{2+} : Co^{III}_2) with a slight excess of reductant were allowed to react at 20 °C until no further u.v.–

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[7] R. S. Bottei and W. A. Joern, *J. Amer. Chem. Soc.*, 1968, **90**, 297.

[8] Los Alamos Report LA 2367, 1959, and addenda by R. H. Moore and R. K. Ziegler. We are grateful to Professor T. W. Newton for sending us details of this program.

visible spectrophotometric changes were observed. The solutions (10 cm^3; $[\mathrm{Cr}^{2+}] = 0.0077$, $[\mathrm{Co^{III}}_2] = 0.0038$, $[\mathrm{H}^+] = 0.1$ mol dm^{-3}, and a second mixture with identical Cr^{2+} and complex concentrations but $[\mathrm{H}^+] = 1.0$ mol dm^{-3}) were diluted to 200 cm^3, and 100-cm^3 samples (duplicate experiments) were loaded on to separate Sephadex SP C-25 columns (the resin was in the H^+ form). The following bands were eluted off the column with $\mathrm{HClO_4}$–$\mathrm{Li[ClO_4]}$ mixtures: pink $[\mathrm{Co(OH_2)_6}]^{2+}$, blue $[\mathrm{Cr(OH_2)_5(Hacd)}]^{2+}$, grey $[\mathrm{Cr(OH_2)_6}]^{3+}$, and a chromium(III) species with an apparent charge $>3+$, most probably $4+$. The visible spectrum of the latter had maxima at (absorption coefficients are per chromium atom, dm^3 mol^{-1} cm^{-1}): 414 (27) and 572 nm (24). Incorporation of acd was shown by base hydrolysis of solutions containing only this species and diethyl ether extraction of re-acidified solutions. Free acd was recovered from the ether phase. Similarly, the mononuclear $[\mathrm{Cr^{III}(Hacd)}]$ species was shown to contain co-ordinated acd. The visible spectrum is very similar to that observed for the binuclear $[\mathrm{Cr^{III}(acd)Cr^{III}}]$ product and had maxima at 412 (25) and 568 nm (ε 23 dm^3 mol^{-1} cm^{-1}). The product distribution was dependent on the initial $[\mathrm{H}^+]$: reaction solutions with $[\mathrm{H}^+] = 0.1$ mol dm^{-3} yielded *ca.* 50% of the total chromium as $[\mathrm{Cr^{III}(acd)Cr^{III}}]$ {22% $[\mathrm{Cr^{III}(Hacd)}]$ and 27% $[\mathrm{Cr(OH_2)_6}]^{3+}$}, whereas from solutions with $[\mathrm{H}^+] = 1.0$ mol dm^{-3} only 25% of the binuclear species was obtained {38% of $[\mathrm{Cr^{III}(Hacd)}]$ and 37% of $[\mathrm{Cr(OH_2)_6}]^{3+}$}. It was shown that the formation of mononuclear chromium(III) products may be due at least in part to an acid- and chromium(II)-catalyzed aquation of the binuclear $[\mathrm{Cr^{III}(acd)Cr^{III}}]$ complex. A primary source of the mononuclear chromium(III) products could arise from reduction of the proposed intermediate complex $[\mathrm{Co^{III}(acd)Cr^{III}}]$ (see Scheme) by the second Cr^{2+} *via* the aqua-ligands of $\mathrm{Co^{III}}$, and/or *via* attack of the second Cr^{2+} at the carbonyl oxygen remote from the cobalt(III) centre. A detailed study of the decomposition of the $[\mathrm{Cr^{III}(acd)Cr^{III}}]$ species and the resulting product distribution was not attempted since it was felt that the mere existence of such a binuclear chromium(III) complex is strong evidence for an inner-sphere mechanism for the reduction of the first cobalt(III) centre of complex (I) (at least of the unprotonated form).

TABLE 1

Kinetic data for the first stage of the Cr^{2+} reduction of complex (I) at $I = 1.0$ mol dm^{-3} ($\mathrm{Li[ClO_4]}$)

θ_c	$[\mathrm{H}^+]$	$10^2[\mathrm{Cr}^{2+}]$	$10^3[\mathrm{Co^{III}}_2]$	k_0
°C		mol dm^{-3}		dm^3 mol^{-1} s^{-1}
4.8	0.01	6.70	0.5	0.065
	0.03	6.05	1.0	0.071
	0.05	6.18	1.0	0.090
	0.10	6.18	1.0	0.116
	0.30	6.17	1.0	0.173
	0.50	6.90	1.0	0.200
	0.65	6.90	1.0	0.225
14.9	0.01	6.54	0.5	0.103
	0.05	7.03	0.5	0.137
	0.10	6.18	1.0	0.165
	0.30	6.03	1.0	0.255
	0.50	6.33	1.0	0.313
	0.79	7.15	1.0	0.346
20.0	0.03	6.20	1.0	0.147
	0.10	6.13	1.0	0.211
	0.20	6.05	1.0	0.271
	0.40	6.26	1.0	0.334
	0.50	6.18	1.0	0.353
25.0	0.025	10.61	1.0	0.176
	0.05	7.26	1.0	0.195
	0.10	2.36	0.5	0.244
	0.10	6.31	1.5	0.246
	0.20	3.65	1.0	0.308
	0.30	3.70	0.5	0.372
	0.30	13.76	2.0	0.374
	0.50	5.28	1.0	0.432
	0.50	10.38	2.0	0.431
	0.65	7.41	1.0	0.444
	0.80	2.42	0.5	0.454
35.0	0.01	7.03	0.5	0.235
	0.05	6.19	1.0	0.314
	0.10	7.25	0.5	0.376
	0.20	7.43	0.5	0.442
	0.30	7.09	0.5	0.510
	0.40	6.20	1.0	0.517
	0.65	6.09	1.0	0.654

Reduction of the Di-μ-hydroxo-μ-(methoxycarbonylacetylenecarboxylato-OO′)-bis[triamminecobalt(III)], (II), *by* Cr^{2+} *and* V^{2+}.—The stoicheiometry of the reduction of complex (II) by Cr^{2+} was 2 : 1 ($\mathrm{Cr}^{2+} : \mathrm{Co^{III}}_2$) as in (1). A very slow second stage of the reaction with reduction of the C≡C triple bond does not interfere with rapid reduction of two cobalt(III) centres and was not studied in any detail. A strictly first-order dependence on reductant was observed for the first stage of the reduction, and the rate was independent of acid concentration (0.1—0.9 mol dm^{-3}) according to rate law (3) with the reductant in large excess over the oxidant. Reduction of the first $\mathrm{Co^{III}}$ is again rate determining. Second-order rate constants are listed in Table 2, and the kinetic

$$-\mathrm{d}\ln[\mathrm{Co^{III}}_2]/\mathrm{d}t = k_{\mathrm{Cr}}[\mathrm{Cr}^{2+}] \qquad (3)$$

parameters are summarized in Table 3. Characterization of the various reaction products was not attempted. Conceivable ester hydrolysis accompanying electron transfer was not investigated because the aim of the present experiments was merely to establish a possible dependence of the rate of reduction on $[\mathrm{H}^+]$ (see below).

TABLE 2

Second-order rate constants for the reduction of complex (II) by Cr^{2+} at I 1.0 mol dm^{-3} ($\mathrm{Li[ClO_4]}$)

θ_c	$[\mathrm{H}^+]$	$10^2[\mathrm{Cr}^{2+}]$	$10^3[\mathrm{Co^{III}}_2]$	k_{Cr}
°C		mol dm^{-3}		dm^3 mol^{-1} s^{-1}
3.7	0.21	3.99	1.0	0.152
	0.21	7.27	1.0	0.155
	0.21	9.75	1.0	0.152
	0.22	14.26	1.0	0.153
14.2	0.21	4.00	1.0	0.214
	0.21	7.24	1.0	0.218
	0.21	10.63	1.0	0.214
	0.22	15.17	1.0	0.221
25.0	0.10	3.08	0.5	0.304
	0.10	3.91	0.5	0.307
	0.20	3.84	0.5	0.278
	0.20	15.67	0.5	0.304
	0.40	12.39	1.0	0.303
	0.40	9.46	1.0	0.337
	.060	6.09	0.2	0.308
	0.60	0.97	0.2	0.298
	0.91	3.38	0.5	0.293
	0.91	2.89	0.5	0.311
36.1	0.21	6.71	1.0	0.483
	0.21	10.40	1.0	0.477
	0.21	15.07	1.0	0.478

The reduction of complex (II) by V^{2+} was studied at 25 °C under pseudo-first-order conditions (excess of reductant) and was found to be independent of $[\mathrm{H}^+]$ conforming to rate law (4). Reduction of the first $\mathrm{Co^{III}}$ is rate

$$-\mathrm{d}\ln[\mathrm{Co^{III}}_2]/\mathrm{d}t = k_{\mathrm{V}}[\mathrm{V}^{2+}] \qquad (4)$$

determining. Rate data are listed in Table 6. The ratio of the second-order rate constants (25 °C, $I = 1.0$ mol dm^{-3}), $k_{Cr} : k_V = 0.82 : 1$, is certainly not in line with values predicted for outer-sphere reductions of a common oxidant (0.02). It is proposed that the V^{2+} reduction of complex (II) proceeds by an outer-sphere mechanism[9] and the Cr^{2+} reduction *via* an inner-sphere mechanism with attack of the reductant at the remote carbonyl oxygen atom.

TABLE 3

Summary of kinetic parameters for the first step of the Cr^{2+} reductions of complexes (I)—(IV) at 25 °C and $I = 1.0$ mol dm^{-3} (Li[ClO$_4$])

Complex		k / dm^3 mol^{-1} s^{-1}	$\Delta H^‡$ / kcal mol^{-1}	$\Delta S^‡$ / cal K^{-1} mol^{-1}	Mechanism
(I)	k_a	0.668 ± 0.008	4.8 ± 0.2	−41.5 ± 0.7	i.s. Remote attack
	k_b	0.127 ± 0.01	7.2 ± 0.8	−38.1 ± 2.5	i.s. Remote attack
(II)		0.321 ± 0.003	5.7 ± 0.2	−41.8 ± 0.6	i.s. Remote attack
(III)		(1.06 ± 0.13) × 10^{-2}			o.s.
(IV)		(4.37 ± 0.14) × 10^{-3}			o.s.

i.s. = Inner sphere, o.s. = outer sphere; 1 cal = 4.184 J.

Reduction of the Tetranuclear Complex (III) *and the μ-Propiolato-complex* (IV) *by* Cr^{2+} *and* V^{2+}.—Spectrophotometric measurements of reaction mixtures containing a tenfold excess of Cr^{2+} at 715 nm {absorption maximum of $[Cr(OH_2)_6]^{2+}$} over complex (III) indicate the stoicheiometry of the reaction to be 6 : 1 (5.9 ± 0.3 mol of Cr^{2+} to 1 mol of complex). This is consistent with 4 Co^{III} being reduced to Co^{II} and the triple bond to a C=C double-bond. Fumaric acid was in fact shown to be a product of the reaction by diethyl ether extraction of base-hydrolysed reaction mixtures. The change in absorbance of the solutions ($[H^+] = 0.2$, $[Cr^{2+}] = 0.016$, [complex] = 0.001 mol dm^{-3}) was followed spectrophotometrically at 524 nm (absorption maximum of complex) and at 715 nm [no absorption of complex (III)]. The initial absorbance values after mixing of the reactants corresponded to predicted values. Only one stage of the reaction was detected and the measured rate constants were, within experimental error, identical for determinations at the two different wavelengths. This indicates that reduction of the first Co^{III} is rate determining and that Cr^{2+} does not reduce the C≡C triple-bond in a fast step prior to the reduction of Co^{III}. A strict first-order

$$-\mathrm{d}\ln[\mathrm{Co^{III}}_4]/\mathrm{d}t = k_{Cr}[Cr^{2+}] \qquad (5)$$

dependence on reductant was observed as in (5). Second-order rate constants are listed in Table 4. The rate law is in support of the above interpretation since it is reported that reduction of acetylene by Cr^{2+} exhibits a second-order dependence on $[Cr^{2+}]$ and a first-order dependence on $[H^+]$.[10]

A similar procedure was adopted for the study of the reduction of complex (IV) by Cr^{2+}. The stoicheiometry was 4 : 1 [3.9 ± 0.3 mol of Cr^{2+} to 1 mol of complex (IV)] corresponding to the reduction of 2Co^{III} and the triple-bond. Attempts to isolate and characterize the reduced form of the organic ligand were not successful, possibly due to polymerization of acrylic acid which is assumed to be the first reduced product of propiolic acid. Again only one step of the reaction is kinetically relevant, and it is concluded that this step corresponds to the reduction of 2Co^{III}, reduction of the first of which is rate determining. The reaction was independent of $[H^+]$ and followed a rate law as in (3). Again the reaction is relatively slow. Second-order rate constants are given in Table 4.

In order to help with the assignment of outer-sphere mechanisms for the reactions of complexes (III) and (IV) with Cr^{2+}, a brief kinetic investigation of the reduction of these complexes with V^{2+} at 25 °C and $I = 1.0$ mol dm^{-3} (Li[ClO$_4$]) was initiated. The reactions were independent of $[H^+]$, reduction of the first Co^{III} being rate determining. A strictly first-order dependence on reductant was observed as in (6). Rate data are listed in Table 5. No evidence for the interaction of V^{2+} with the C≡C triple-bond prior to reduction of the first Co^{III} was found.

TABLE 4

Second-order rate constants for the Cr^{2+} reduction of complexes (III) and (IV) at 25 °C and $I = 1.0$ mol dm^{-3} (Li[ClO$_4$])

Complex	$[H^+]$ / mol dm^{-3}	$10^2[Cr^{2+}]$ / mol dm^{-3}	10^3[complex] / mol dm^{-3}	$10^2 k_{Cr}$ / dm^3 mol^{-1} s^{-1}
(III)	0.13	14.39	1.0	1.23
	0.16	16.30	0.5	1.17
	0.20	2.59	0.5	0.94
	0.20	4.67	3.0	0.96
	0.40	1.09	0.5	1.25
	0.40	4.34	0.5	0.99
	0.40	8.55	0.5	1.07
	0.60	6.66	0.5	1.05
	0.60	12.71	0.5	1.12
			Average:*	1.09 ± 0.12
(IV)	0.14	18.05	0.5	0.432
	0.20	7.42	2.0	0.411
	0.30	9.78	1.0	0.435
	0.40	3.67	0.5	0.443
	0.40	7.56	0.5	0.450
	0.40	10.28	0.5	0.432
	0.60	9.21	1.0	0.453
			Average:*	0.437 ± 0.014

* Error limits are the standard deviations.

$$-\mathrm{d}\ln[\text{complex}]/\mathrm{d}t = k_V[V^{2+}] \qquad (6)$$

DISCUSSION

The observed rate law for the reduction of complex (I) by Cr^{2+} and the detection of a binuclear chromium(III) product which contains the organic ligand are consistent with an inner-sphere mechanism with remote attack of the first Cr^{2+} at the uncomplexed (unprotonated) carboxyl group. The results of the product analysis do not allow an unambiguous assignment of an inner-sphere mechanism to the reduction of the protonated form. However, it is noted that the rate and the activation parameters of the reduction of the protonated form of complex (I) are very similar to those observed for the unprotonated form. It is concluded that the protonated

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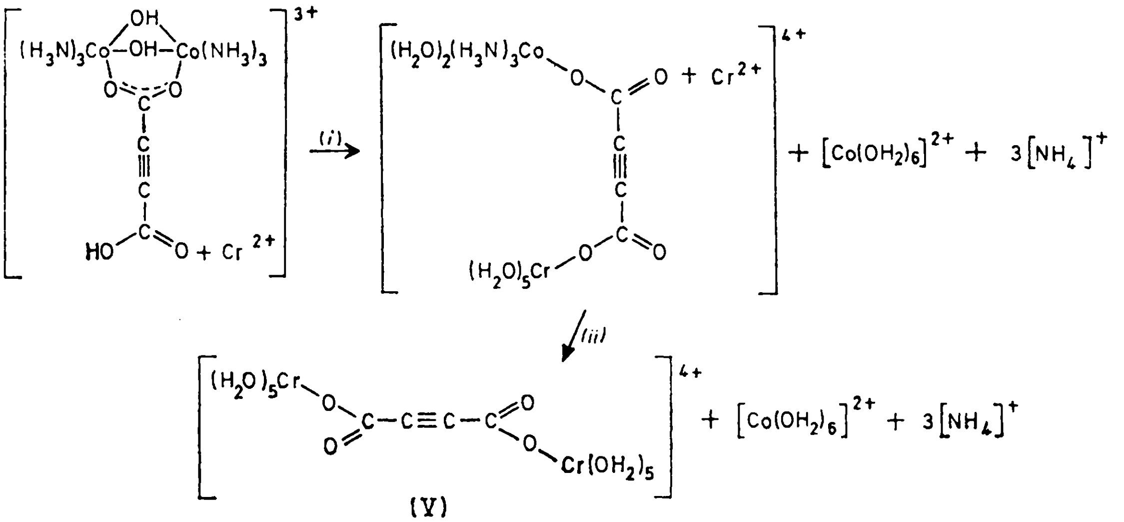
[9] C. Norris and F. R. Nordmeyer, *Inorg. Chem.*, 1971, **10**, 1235.

[10] A. E. Shilov, *Kinetics Catalysis* (*U.S.S.R.*), 1970, **11**, 256.

and unprotonated form react with Cr^{2+} by an inner-sphere mechanism with remote attack.

The proposed binuclear Co^{III}–Cr^{III} intermediate is rapidly reduced by a second Cr^{2+}, at least in part by an inner-sphere mechanism with attack of Cr^{2+} at the carbonyl oxygen atom adjacent to the co-ordinated Co^{III}. The product is a binuclear μ-(acetylenedicarboxylato-$O'O^2$)-bis[penta-aquachromium(III)] complex with a 4+ charge.



SCHEME (*i*) Remote attack, rate determining; (*ii*) adjacent attack, rapid

Alternate paths for the reduction of the intermediate would be *via* attack of Cr^{2+} at the aqua-ligands of Co^{III} and *via* attack at the carbonyl oxygen remote from Co^{III}. Hexa-aquachromium(III) and $[Cr(OH_2)_5(Hacd)]^{2+}$ would be the Cr^{III} products. From our ion-exchange experiments it is not possible to discern these reaction paths because ready aquation of the binuclear chromium(III) complex occurs.

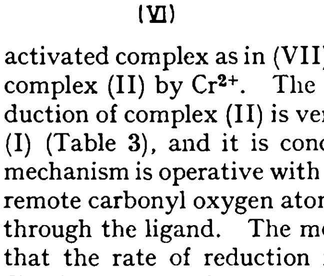
TABLE 5

Second-order rate constants for the reduction of complexes (II)—(IV) by V^{2+} at 25 °C and I = 1.0 mol dm^{-3} (Li[ClO$_4$])

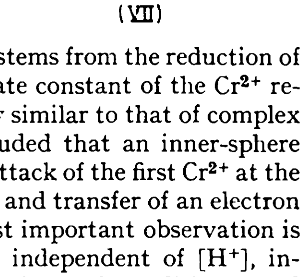
Complex	[H$^+$]	$10^2[V^{II}]$	10^3[complex]	k_V
	mol dm^{-3}			dm^3 mol^{-1} s^{-1}
(II)	0.072	3.52	0.5	0.388
	0.072	6.47	1.0	0.361
	0.08	6.49	0.4	0.369
	0.50	8.37	0.5	0.368
	0.65	3.48	0.2	0.384
	0.78	1.07	0.2	0.348
	0.78	6.69	0.5	0.360
			Average:*	0.37 ± 0.02
(III)	0.10	1.52	0.5	0.550
	0.10	2.90	0.5	0.537
	0.12	4.77	1.0	0.541
	0.22	4.80	1.0	0.536
	0.50	2.31	0.5	0.563
	0.50	4.02	0.7	0.554
	0.80	9.34	0.5	0.583
	0.80	1.45	1.0	0.568
			Average:*	0.55 ± 0.02
(IV)	0.12	4.95	1.0	0.263
	0.12	8.12	0.5	0.232
	0.50	6.82	2.0	0.230
	0.80	3.17	0.5	0.249
	0.80	1.47	0.5	0.241
			Average:*	0.24 ± 0.01

* Errors limits are the standard deviations.

Electron transfer through the C≡C triple-bond of complex (I) appears to be enhanced by protons. Therefore, the site of protonation in the activated complex is of interest. As indicated by the measured protonation constant (K = 2.1 dm^3 mol^{-1} at 25 °C and I = 1.0 mol dm^{-3}), complex (I) is a strong acid with a carboxylate group and a weakly basic C≡C triple-bond representing two possible sites of protonation. Thus two different activated complexes for the reduction of the protonated form of complex (I) are conceivable. Evidence for an activated complex as in (VII) stems from the reduction of complex (II) by Cr^{2+}. The rate constant of the Cr^{2+} reduction of complex (II) is very similar to that of complex (I) (Table 3), and it is concluded that an inner-sphere mechanism is operative with attack of the first Cr^{2+} at the remote carbonyl oxygen atom and transfer of an electron through the ligand. The most important observation is that the rate of reduction is independent of [H$^+$], indicating that under the experimental conditions used protonation at the triple-bond does not occur (or is kinetically not relevant to the rate of reduction). It is noted that an activated complex with protonation at the carbonyl oxygen is generated when the protonated form



(VI)



(VII)

of the di-μ-hydroxo-μ-oxalato-bis[triamminecobalt(III)] complex is reduced by Cr^{2+}.[11]

Since it is known that certain metal aqua-ions co-ordinate strongly to unsaturated carbon–carbon bonds in aqueous acidic solutions,[12] the possibility of $[Cr(OH_2)_6]^{2+}$ binding directly at the triple-bonds of complexes (I) and (II) must be considered an alternative point of attack of the reductant. In order to clarify the situation the kinetics of the reductions of complexes (III) and (IV) by Cr^{2+} and V^{2+} were studied. The rate of reduction of the tetranuclear complex (III) by Cr^{2+} is slow compared to the corresponding rates of complexes (I) and (II). It is possible to assign outer-sphere mechanisms for the Cr^{2+} and V^{2+} reductions of this complex using the well established linear free-energy relation[13] correlating outer-sphere rate constants for reductions with Cr^{2+} and V^{2+}. The ratio of the second-order rate constants for reductions of complex (III), $k_{Cr} : k_V$, is 0.020 : 1 (Tables 4 and 5), which is in excellent agreement with other known outer-sphere reactions.[13] Thus co-ordination of all four oxygen atoms of acd to cobalt(III) centres enforces an outer-sphere mechanism, and no evidence for bonding of Cr^{2+} at the C≡C triple-bond and succeeding electron transfer was found. This conclusion is bolstered by the fact that the reductions of complex (IV) by Cr^{2+} and V^{2+} occur by outer-sphere mechanisms, respectively ($k_{Cr} : k_V = 0.018 : 1$), since in this instance the triple-bond would be sterically easily accessible to the reductant (it ' sticks out ' of the complex cation) whereas in complex (III) a second bulky di-μ-hydroxo-bis[triamminecobalt(III)] group might exercise some steric hindrance.

TABLE 6

Comparison of kinetic parameters for the Cr^{2+} reductions of selected binuclear and tetranuclear di-μ-hydroxo-bis[triamminecobalt(III)] complexes with dicarboxylato-bridging ligands at 25 °C and $I = 1.0$ mol dm^{-3} (Li[ClO$_4$])

Carboxylic acid		k dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1} mol^{-1}	Mechanism	Ref.
Oxalic	k_a	4.68	9.04	−25.1	i.s.	*a*
	k_b	131.0	6.3	−27.9	i.s.	
b		0.003 6	8.2	−42.1	o.s.	*c*
Malonic		0.002 65			o.s.	6
Maleic		1.87 [d]	4.3	−43.0	i.s.	5
Fumaric		2.64 [d]	2.8	−47.1	i.s.	5

J. Baldea, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, submitted for publication. [b] Tetranuclear μ-oxalato-complex. [c] K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1973, 736. [d] k_b; the path for the unprotonated form was not detected.

In summary, complex (I) is reduced by Cr^{2+} *via* an inner-sphere mechanism with attack of the first Cr^{2+} at the protonated or unprotonated, uncomplexed, carboxyl group and transfer of an electron through the C≡C triple-bond. It is noted that the protonated form reacts faster than the deprotonated form despite the fact that only one oxygen of the carboxyl group is available for precursor complex formation with Cr^{2+} (statistical factor), and despite the higher positive charge of the protonated form (this would effect the precursor formation constant since two positively charged species are reacting). For the analogous μ-oxalato-complex (Table 6) the reverse behaviour is observed. It is not possible for us to offer a plausible explanation of the role of the protons, because it is difficult to see how a proton which is attached to the same carboxylic function as the reductant can improve the conjugation and/or the reducibility of the ligand at one time and deteriorate it at another.[14]

In Table 6 kinetic data for the Cr^{2+} reductions of a variety of di-μ-hydroxo-bis[triamminecobalt(III)] complexes with dicarboxylato-ligands are compiled. Comparison of the rate data for the inner-sphere reduction of the protonated form of complex (I) (Table 3) with those of the corresponding μ-fumarato- (and maleato-) complex reveals that electron transfer through the C=C double-bond appears to be 3—4 times faster than through the C≡C triple-bond. The reduction of these complexes involves formation of trinuclear Co^{III}_2–Cr^{II} precursor complexes. Therefore, the measured rate constants are a function of the precursor complex-formation constant, K_f, and the intrinsic electron-transfer rate constant, k_{et}: $k_{Cr} = k_{et}K_f$. Because the steric requirements for the formation of the precursor complexes are identical for both oxidants, it is assumed that the formation constants, K_f, are identical,[15] and the observed differences in rates may be due to differing electron-transfer rate constants, k_{et}. It is known that the uncomplexed acd is easily reduced by Cr^{2+} yielding fumaric acid,[7] whereas fumaric acid is only slowly reduced to succinic acid.[16,17] Based on the differing reducibilities alone, a faster rate of reduction for complex (I) would be expected.[18] However, C≡C triple bonds delocalize π electrons to a lesser extent than C=C double bonds. Therefore, we propose that

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[11] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

[12] J. K. Hurst and R. H. Lane, *J. Amer. Chem. Soc.*, 1973, **95**, 1703.

[13] See, for example, ref. 1 and J. C. Chen and E. S. Gould, *J. Amer. Chem. Soc.*, 1973, **95**, 5544 and D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2635; for binuclear cobalt(III) ammine complexes a detailed account is given by J. Baldea, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, to be submitted for publication.

[14] H. Taube, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 967.

[15] This assumption is based mainly on the observation that Cr^{2+} reduction rates of sterically equivalent $Co^{III}(NH_3)_5$ carboxylato-complexes are nearly identical and not sensitive to inductive effects which vary the basicity of the adjacent carbonyl oxygen atom: M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 1971, **10**, 1318.

[16] A. Malliaris and D. Katakis, *J. Amer. Chem. Soc.*, 1965, **87**, 3077.

[17] E. Vrachnou-Astra, P. Sakellaridis, and D. Katakis, *J. Amer. Chem. Soc.*, 1970, **92**, 811, 3936.

[18] H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.

despite more favourable reducibility a triple-bond is not as efficient an electron-mediating structural unit as a double-bond because of reduced conjugation.

EXPERIMENTAL

Preparations.— *μ-(Carboxyacetylenecarboxylato-OO′)-di-μ-hydroxo-bis[triamminecobalt*(III)*] perchlorate*, (I). To a solution of H_2acd (10 g, 0.09 mol) in aqueous 0.5 mol dm^{-3} perchloric acid (50 cm^3) at 45 °C, tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate (10 g) (hereafter referred to as the tri-μ-hydroxo-complex) was added in small amounts with stirring. The temperature was increased to 65 °C and was maintained for 15 min. Concentrated $HClO_4$ (10 cm^3) was slowly added to the cooled and filtered solution which was kept at 0 °C for a few hours. The resulting red crystals (very thin needles) were collected and washed with absolute ethanol and diethyl ether. The solid was recrystallized from a minimum of water (35 °C) and concentrated $HClO_4$ {Found: C, 7.2; H, 3.7; Cl, 15.6; Co, 17.0; N, 12.3. Calc. for $[(H_3N)_3Co(OH,OH,C_4HO_4)Co(NH_3)_3][ClO_4]_3{\cdot}H_2O$: C, 7.0; H, 3.4; Cl, 15.6; Co, 17.2; N, 12.3%}. The u.v. spectrum had maxima at 524 (ε 110) and 300 nm (ε 2.6 × 10^3 dm^3 mol^{-1} cm^{-1}). The i.r. spectrum exhibited C–O stretching frequencies of a complexed μ-carboxylato-group at 1 565 and 1 390 cm^{-1} and an uncomplexed protonated carboxyl group at 1 718 and 1 325 cm^{-1}.

Addition of solid Na[ClO$_4$] to a concentrated and neutralized (0.5 mol dm^{-3} Na[OH]) solution of complex (I) yielded a deprotonated form as a solid which is extremely soluble in water and was not obtained analytically pure. However, the i.r. spectrum showed two ν(C–O) bands for an uncompleted and deprotonated carboxyl group at 1 620 and 1 325 cm^{-1} in addition to two bands of complexed carboxylate at 1 575 and 1 390 cm^{-1}.

Di-μ-hydroxo-μ-(methoxycarbonylacetylenecarboxylato-OO′)-bis[triamminecobalt(III)*] perchlorate*, (II). Preparation of the monomethyl ester of H_2acd could not be found in the literature; the method used involved partial hydrolysis of the diester.[19] To a solution of the dimethyl ester of H_2acd (28.4 g) in ethanol (50 cm^3) and water (50 cm^3), a solution of Na[OH] (8 g) in ethanol (50 cm^3) was added dropwise with stirring at room temperature. During the reaction a white crystalline precipitate formed (the disodium salt of H_2acd) which was filtered off and discarded. The resulting solution was acidified with 5 mol dm^{-3} $HClO_4$ (50 cm^3) and extracted three or four times with diethyl ether. The ether solution was dried over Mg[SO$_4$]. Diethyl ether and ethanol were then removed under reduced pressure at 40 °C. A pale yellow liquid containing the monomethyl ester of H_2acd was obtained. The crude product was used without further purification or characterization. The above liquid (5 cm^3) was allowed to react with the tri-μ-hydroxo-complex (6 g) 0.5 mol dm^{-3} $HClO_4$ (35 cm^3) and dioxan (50 cm^3) at 60 °C for 10—15 min. Solid Na[ClO$_4$] and concentrated $HClO_4$ (5 cm^3) were added. The solution was allowed to stand in a draughty fume cupboard for 2 d. Very thin crystals (needles) were collected and washed with ethanol and diethyl ether {Found: C, 8.0; H, 3.7; Cl, 14.9; Co, 16.6; NH$_3$, 14.5. Calc. for $[(H_3N)_3Co(OH,OH,C_5H_3O_4)Co(NH_3)_3][ClO_4]_3{\cdot}2H_2O$: C, 8.4; H, 3.8; Cl, 14.9; Co, 16.5; NH$_3$, 14.3%}. U.v.—visible spectrum: $\lambda_{max.}$ = 524 (111), 370 (sh) (248), and 302 nm (ε 2.7 × 10^3 dm^3 mol^{-1} cm^{-1}). I.r. spectrum: ν_{asym} (C–O) at 1 555 cm^{-1} and ν_{sym} (C–O) at 1 395 cm^{-1} of complexed carboxylate, and two ν(C–O) stretching frequencies of the methyl ester group at 1 712 and 1 290 cm^{-1}.

μ-(Acetylenedicarboxylato-$O^1O^{1\prime}$:$O^2O^{2\prime}$*)-bis{di-μ-hydroxo-bis[triamminecobalt*(III)*]}perchlorate*, (III). To a solution of H_2acd (0.3 g) in 0.5 mol dm^{-3} $HClO_4$ (15 cm^3) at 45 °C was added the tri-μ-hydroxo-complex (3.0 g). The temperature was increased to 65 °C and maintained for 10 min. Concentrated $HClO_4$ (2 cm^3) and solid Na[ClO$_4$] were added to the cooled (15 °C) and filtered solution which was then kept at 0 °C for a few hours. Red crystals were collected and washed with ethanol and diethyl ether. Recrystallization was from a minimum amount of water with concentrated $HClO_4$ and solid Na[ClO$_4$] {Found: C, 3.8; H, 4.0; Cl, 16.2; Co, 17.7; N, 12.6. Calc. for $[Co_4(NH_3)_{12}(\mu\text{-}OH)_4(\mu\text{-}C_4O_4)][ClO_4]_6{\cdot}5H_2O$: C, 3.7; H, 3.8; Cl, 16.3; Co, 18.0; N, 12.9%}. U.v.–visible spectrum: $\lambda_{max.}$ = 524 nm (214) and 300 nm (ε 5.5 × 10^3 dm^3 mol^{-1} cm^{-1}). This complex exhibited only two ν(C–O) stretching frequencies of complexed carboxyl groups at ν_{asym} 1 578 and ν_{sym} 1 395 cm^{-1}.

Di-μ-hydroxo-μ-(propiolato-OO′)-bis[triamminecobalt(III)*] perchlorate*, (IV). This complex was prepared by the same method as described for (I). Propiolic acid (3 cm^3) was allowed to react with the tri-μ-hydroxo-complex (10 g) in aqueous 0.5 mol dm^{-3} $HClO_4$ (50 cm^3) {Found: C, 5.8; H, 3.7; Cl, 16.4; Co, 18.6; NH$_3$, 16.0. Calc. for $[(H_3N)_3Co(OH,OH,C_3HO_2)Co(NH_3)_3][ClO_4]_3{\cdot}H_2O$: C, 5.6; H, 3.6; Cl, 16.6; Co, 18.4; NH$_3$, 16.0%}. U.v.–visible spectrum: $\lambda_{max.}$ = 524 (106), 370 (sh) (260), and 300 nm (ε 2.7 × 10^3 dm^3 mol^{-1} cm^{-1}). I.r. data: $\nu(C{\equiv}C)$ at 2 105, ν_{asym}(C–O) at 1 540, and ν_{sym}(C–O) at 1 399 cm^{-1}.

Stability of Complexes in Solution.—The stability of complexes (I)—(IV) in acidic aqueous solution was checked spectrophotometrically. No spectral changes were detected in complex solutions (10^{-3} mol dm^{-3}) at two different [H$^+$] (1.0 and 0.1 mol dm^{-3}) for at least 48 h at 30 °C.

Reagents.—The starting complex for the preparation of the present series of carboxylato-complexes is tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate.[20] Acetylenedicarboxylic acid (H_2acd) and the corresponding dimethyl ester were purchased from Merck and were used without further purification. Lithium perchlorate was prepared from lithium carbonate and perchloric acid, and was recrystallized until free from trace amounts of anion impurities. Solutions of chromium(II) perchlorate and vanadium(II) perchlorate were prepared electrolytically under strict air-free conditions from hexa-aquachromium(III) or vanadium(IV) perchlorate in perchloric acid. Chromium(III) perchlorate was prepared by reduction of CrO_3 with H_2O_2 in dilute $HClO_4$. Vanadium(IV) perchlorate was prepared from a saturated solution of vanadium(IV) sulphate using an ion-exchange procedure.

Kinetic Measurements.—The reductions of complexes (I)—(IV) by Cr^{2+} and V^{2+} were studied by conventional spectrophotometric methods using a Unicam SP 1700 spectrophotometer. The reactants were mixed by using standard syringe techniques under an argon or nitrogen atmosphere. All the kinetic experiments were under pseudo-first-order conditions (reductant in at least tenfold excess over oxidant). The decrease in absorbance at 524 nm (maximum absorbance of Co^{III}) was recorded as a function of time. Pseudo-first-order rate constants were evaluated from the gradients (× 2.303) of plots of log ($D_t - D_\infty$) against time, where D_t is the absorbance at

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[19] D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1286.

[20] M. Linhard and H. Siebert, *Z. anorg. Chem.*, 1969, **364**, 24.

time t and D_{∞} that after 8—10 half-lives of the reaction. The ionic strength was adjusted to unity in all the experiments using $Li[ClO_4]$ as supporting electrolyte.

Ion-exchange Separations.—In order to elute highly charged binuclear chromium(III) species, ion-exchange experiments were carried out using Sephadex SP C-25 resin in the H^+ form. Chromium concentrations were determined spectrophotometrically as chromate, and Co^{II} as an intensely coloured complex with 2-hydroxy-1-nitrosonaphthalene-3,6-disulphonic acid.[21]

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[21] K. J. McNaught, *Analyst*, 1942, **67**, 97.